

Order-disorder transition and alignment dynamics of a block copolymer under high magnetic fields by in situ x-ray scattering

Manesh Gopinadhan,^{*} Paweł W. Majewski,[†] and Chinedum O. Osuji[‡]

Department of Chemical and Environmental Engineering, Yale University, New Haven CT 06511
(Dated: July 9, 2012)

We present results of temperature resolved scattering studies of a liquid crystalline block copolymer undergoing an order-disorder transition (ODT) in the presence of magnetic fields and time-resolved measurements during isothermal field annealing at sub-ODT temperatures. In each case, field interactions produced strongly textured mesophases with the cylindrical microdomains aligned parallel to the field. We find there is no measurable field-induced shift in the ODT temperature (T_{ODT}) which suggests that selective melting does not play a role in mesophase alignment during isothermal experiments. Our data indicate instead that sub-ODT alignment occurs by slow, large scale grain rotation whereas alignment during cooling from the disordered melt is rapid and driven by the nucleation of weakly ordered but preferentially aligned material. We identify an optimum sub-cooling that maximizes alignment during isothermal field annealing. This is corroborated by a simple model incorporating the competing effects of an exponentially decreasing mobility and divergent, increasing magnetic anisotropy on cooling below T_{ODT} . The absence of measurable field-effects on T_{ODT} is consistent with rough estimates derived from the relative magnitudes of the free energy due to field interaction and the enthalpy of the isotropic-LC transition.

PACS numbers: 83.80.Uv, 61.30.Vx, 64.75.Yz

Self-assembly on mesoscopic length scales in soft matter gives rise to a fascinating variety of microstructures. Block copolymers (BCPs) are particularly intriguing due to the wide range of morphologies and functionalities that are accessible by appropriate control of chemical composition, chain architecture and molecular weight. Their utilization in various applications is often predicated on the ability to control the orientation of their microstructure. External inputs such as shear flow, electric fields and magnetic fields provide utility in this regard, as well reviewed [1]. Due to the absence of dielectric breakdown concerns and their space pervasive nature, magnetic fields are particularly well suited for this purpose. They effectively permit arbitrary control over grain texture in appropriately field-responsive materials, even in complex geometries [2].

Microstructure alignment by magnetic fields is driven by anisotropy in the system's magnetic susceptibility, $\Delta\chi$, that gives rise to an orientation dependent field interaction energy. Suitably large interactions can dominate thermal forces or other external inputs on timescales dictated by the viscosity of the material. Typical coil-coil BCPs such as poly(styrene-*b*-methyl methacrylate) support vanishingly small anisotropies with $\Delta\chi \mathcal{O}(10^{-9})$ in dimensionless volume SI units. This is due to the short persistence length or random coil nature of the chains and the similarity of the susceptibilities of the component species. The presence of rigid anisotropic moieties such as aromatic mesogens in liquid crystalline (LC) mesophases [3–8] and extended chains in semi-crystalline polymers [9, 10] as well as surfactants [11–13] gives rise to $\Delta\chi \mathcal{O}(10^{-6})$ which is sufficient to drive alignment at readily accessible field strengths of a few tesla. Mag-

netic nanoparticle inclusions can also provide an elegant means for advancing field directed self-assembly of lyotropic mesophases as recently demonstrated [14]. Deliberate incorporation of liquid crystallinity in BCPs can therefore be used as a convenient handle to control microstructure in these systems by magnetic fields. Despite this potential, studies of field driven phase behavior and alignment dynamics in BCPs have been limited. This is in part due to the need for superconducting magnets and the experimental difficulty associated with conducting studies in the presence of high fields.

In this Letter we report on a series of *in situ* scattering studies of an LC BCP under magnetic fields using a custom designed x-ray instrument coupled to a high field magnet. Temperature resolved measurements show no discernible field effects on the order-disorder transition (ODT) of the system. Time resolved experiments on pre-aligned materials show that alignment at sub-ODT temperatures occurs via grain rotation with slow kinetics. The response of the system is critically limited by the mesophase viscosity such that alignment can only be advanced by residence in a small temperature window near T_{ODT} . This residence produces a weakly aligned system which thereafter transitions to a strongly aligned state on cooling, even in the absence of the field. We provide simple models which correctly capture the absence of measurable field-effects on the ODT and the existence of an optimum sub-cooling for the maximization of orientation order parameters in isothermal experiments.

The polymer studied is poly(ethylene oxide-*b*-methacrylate), PEO-PMA/LC in which the methacrylate block is side functionalized using a cyanobiphenyl mesogen (Polymersource Inc.), Fig. 1a. The num-

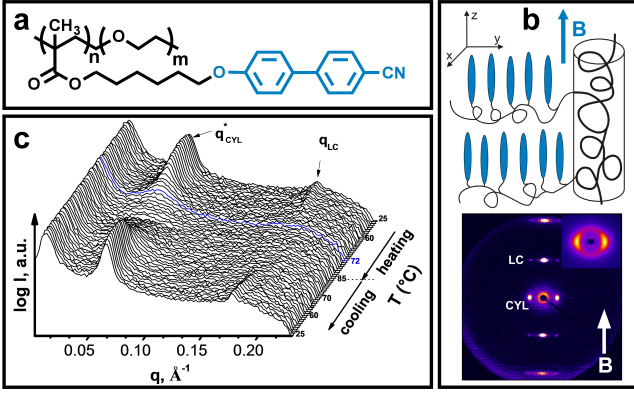


FIG. 1. a: Chemical structure of LC BCP. b: Schematic showing homogeneous anchoring of mesogens at IMDS. Mesogens and PEO cylinders align parallel to the field as shown by associated 2D SAXS and WAXS (inset). c: Temperature resolved SAXS at zero-field. The blue trace marks T_{ODT}

ber average molecular weight M_n is 10.4 kg/mol with PEO weight fraction $f_{PEO}=0.23$ and polydispersity index ≈ 1.1 . The system forms hexagonally packed cylinders of PEO in the PMA/LC matrix, with a d-spacing, $d_{CYL}=9.6$ nm. Samples were prepared by solvent casting from 5 wt.% dimethyl formamide solutions to provide 3 mm diameter discs of 1-2mm thickness. Small angle x-ray scattering (SAXS) measurements were conducted using a custom SAXS bench (Rigaku) integrated with a 6 T cryogen-free magnet (American Magnetics Inc.).

The polymer phase behavior is typical of weakly segregated LC BCPs. DSC (not shown) and zero-field SAXS measurements, Fig. 1c, show that the ODT at ≈ 72 $^{\circ}\text{C}$ is effectively coincident with the nematic-isotropic transition around 69 $^{\circ}\text{C}$. The BCP microphase separation is driven by the change in block interaction that occurs on formation of the nematic mesophase, as observed in analogous LC BCPs [15]. A second transition from nematic to smectic A occurs near 63 $^{\circ}\text{C}$. The cyanobiphenyl mesogens exhibit a homogeneous anchoring condition at the inter-material dividing surface (IMDS) between the PEO and PMA blocks. This implies that the orientation of the cylindrical microdomains will be parallel to that of the mesogens themselves and the periodicity of the smectic layers, $d_{LC}=3.5$ nm, is orthogonal to that of the cylindrical microdomains as in Fig. 1b. Fig. 2 shows plots of the inverse intensity of the scattering peaks from the smectic layers and cylindrical microdomains as functions of inverse temperature. Samples were initially heated to ≈ 85 $^{\circ}\text{C}$, well above T_{ODT} and then cooled at 0.1 $^{\circ}\text{C}/\text{min}$ to room temperature under different field strengths, stopping every 1 $^{\circ}\text{C}$ for 600 s for data collection. The data were fitted using a standard logistic function to determine T_{ODT} and T_{N-SmA} , Fig. 2d. The results show clearly that there is no discernible influence of the field on the phase transition temperatures beyond

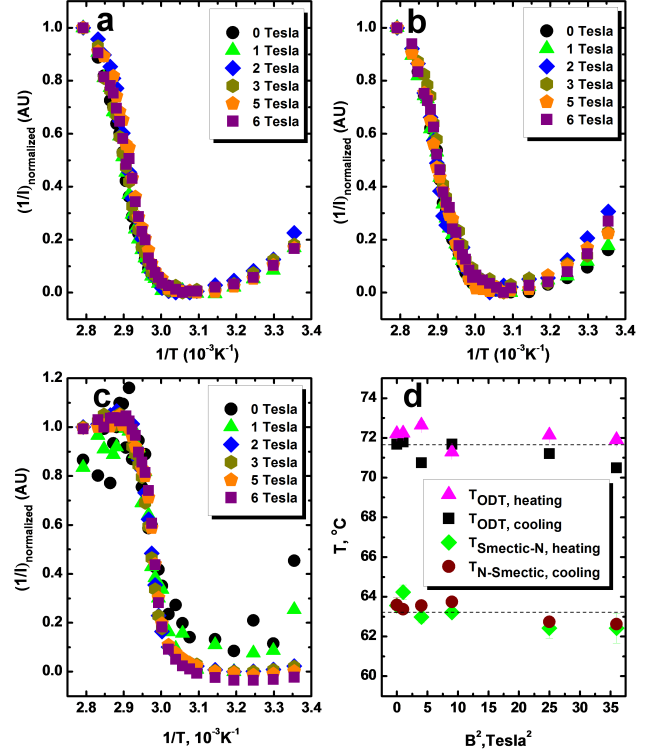


FIG. 2. Inverse peak intensity as a function of $1/T$ for BCP on heating (a) and cooling (b), and for smectic LC scattering on cooling (c). d: T_{ODT} and T_{SmA-N} as a function of B^2 .

the experimental uncertainty of roughly ± 0.5 $^{\circ}\text{C}$ associated with the experimental apparatus. In all cases except the zero-field measurement, the samples displayed alignment of the hexagonally packed cylinders parallel to the field direction. There was pronounced narrowing of the azimuthal intensity distribution (not shown) of the primary scattering peak for field strengths above 2 T, with a saturation of the peak width (FWHM) of roughly 7-8 and 4-5 degrees for the microdomain and smectic layer reflections at $q=0.7$ and 1.8 nm^{-1} respectively.

The role of the field on the isotropic-nematic transition T_{NI} and thus the ODT can be considered through construction of a Clausius-Clapeyron relation incorporating the field interaction energy at constant pressure [16]. The normalized change in transition temperature is given by Eq. 1 where the susceptibility of the nematic state can be closely related to that of the isotropic state and the molecular anisotropy as $\chi_N = \chi_I + (2/3)\Delta\chi_m$, the field interaction energy difference is $(\chi_N - \chi_I)B^2/2\mu_0$ and ΔH_{NI} is the enthalpy associated with the transition.

$$\Delta T/T_{NI} = \frac{\Delta\chi_m B^2}{3\mu_0 \Delta H_{NI}} \quad (1)$$

For the present system, using representative values of $\Delta H_{NI}=1$ J/g (from DSC), $\Delta\chi_m=10^{-6}$ and density $\rho=1$ g/cm 3 , a field strength of 6 T would impose a very small

shift of $\Delta T \approx 4$ mK, which is far below the resolution of the measurements. Such mK-scale shifts are consistent with prior work on electric [17] and magnetic field studies [16] on small molecule LCs. Intriguingly, Segalman *et al.* observed a large 30 K shift in the ODT of a weakly segregated rod-coil block copolymer under application of a 7 T field [18]. It is likely that the small entropy changes associated with ODTs in rod-like systems results in this exceptionally large field effect by comparison with the present side-chain LC BCP and small molecule systems based on analogous cyanobiphenyl mesogens. Conversely Samulski *et al.* examined a system based on a bent-core mesogen with non-trivial transition enthalpies but identified a large 4 K shift in T_{NI} and T_{SmC-N} at 1 T. This was attributed to the presence of partially ordered clusters which couple to the field in this novel class of cybotactic materials [19]. Pronounced field-induced changes in transition temperatures can give rise to selective melting whereby domains which are not in the energy minimizing orientation are destabilized, and thus shrink, or “melt”, and are gradually replaced by aligned material that grows from the disordered melt [20–23]. This acts as an effective mechanism for mesophase alignment. In the present case, given the imperceptible field effects, we can conclude that while selective melting may occur, it does so only over a mK-scale window which cannot be easily leveraged in practice as a viable means of structure control. Correspondingly, this mechanism has little consequence in the current experiments.

The alignment kinetics were probed using isothermal field annealing to monitor microstructure re-orientation at sub-ODT temperatures. A sample was initially well aligned by slowly cooling to room temperature across the ODT at 0.1 °C/min at the highest field strength, 6 T. The field was ramped to 0 T and the sample was physically rotated by 90 degrees around the axis defined by the x-ray beam (x-axis, Fig. 1b) such that in lab-space, the cylindrical microdomains now lay perpendicular to the field direction, i.e. long axes along the y-axis. The field was ramped up to 6 T and the system quickly heated to 67 °C, just below T_{ODT} . Time resolved measurements followed the reorientation of the cylinders from the initial horizontal alignment to the final preferred vertical alignment, parallel to the field and z-axis. The scattering intensity from the hexagonally packed cylinders thus progressively shifted from concentration along the meridional line or z-axis ($\phi=90^\circ$ and 270° azimuthally) to concentration along the equatorial line or y-axis ($\phi=180^\circ$ and 360° azimuthally) and *vice versa* for the smectic layers. The intensity variation of the cylinder microdomain scattering as a function of ϕ and time are shown in Fig. 3, with 2D SAXS diffractograms at pertinent timepoints. Comparison of the initial and final time points (Fig. 3b) indicates that the combined peak intensity is conserved. Likewise, the total scattered intensity integrated across all azimuthal angles at $q=0.7 \text{ nm}^{-1}$ is invariant dur-

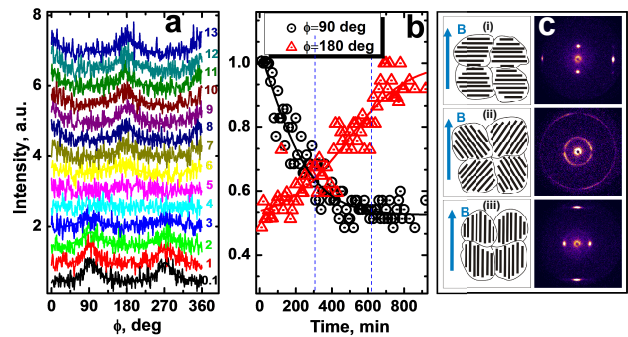


FIG. 3. a: Azimuthal intensity at selected times (hrs). b: Peak intensities at $\phi=90^\circ$ and 180° and exponential fits (lines). c: 2D SAXS and grain reorientation schematics at $t = 0$ (25 °C), $t = 250$ (50 °C) and $t = 900$ min (25 °C).

ing the experiment. This supports the finding from the temperature-resolved study that selective melting is not relevant as such melting would have resulted in a transient overall intensity reduction. We thus conclude that alignment proceeds by grain rotation as shown schematically in Fig. 3c.

Exponential fits of the time traces reveal characteristic times of roughly 400 and 200 minutes for the equatorial rise and meridional decrease of scattering intensity. Consistent with this, at short times there is an initially faster loss of intensity from the 90° peak than the corresponding gain of intensity at the 180° direction. Correspondingly, at long times, the 180° peak continues to gain in intensity while loss at 90° has plateaued. These data clearly indicate that there is an intermediate state via which the system transitions from horizontal to vertically aligned cylinders. This is confirmed by the 2D diffractograms in which 4-fold symmetric chevron like patterns are clearly observed, as shown in inset (ii). To collect this data, the sample was cooled to 50 °C after 250 minutes at 67 °C. This results in increased segregation strength between the blocks and an improvement in the ability to resolve individual scattering peaks which could be smeared out at higher temperature. Such a display of 4-fold symmetric scattering is not unexpected. It is consistent with what is observed experimentally [24] and in simulation [25] during the reorientation of lamellar microdomains under tensile deformation and is clearly the result of the $n=2$ degeneracy with which the system can rotate to re-align with the field - i.e. microdomains can rotate to the right or the left, with equal probability. This appears to be the first observation, however, of the expected 4-fold symmetric chevron-like state from *in situ* experiments in field alignment of block copolymers. Prior work by Böker *et al.* [22, 26] observed an apparent isotropic intermediate state during electric field induced re-alignment, but it is entirely possible that this was the result of peak broadening that blurred the identification of these features in the weak segregation regime in which

the experiment was conducted. The fact that the system here needed to be cooled to 50 °C in order to unambiguously observe the 4-fold intermediate state underscores this point.

The timescale for reorientation is understandably large as rotational motion is severely hindered by the polymer viscosity. In general, alignment of soft mesophases by external fields is advanced on passage across the ODT as this is presumed to maximize the coupling of the field to the system [1]. This is certainly observed empirically, but the underlying physics is a subtle combination of thermodynamic and kinetic contributions. The system's mobility is high near T_{ODT} , but the thermodynamic driving force for alignment is linked to the relevant order parameter, $\Delta\chi$ in the present case, which increases from zero only on passage (cooling) through the ODT. We can construct a simple model describing the alignment kinetics as a function of temperature. We represent $\Delta\chi(T)$ for the first order N-I transition in the conventional Haller approach [27] as $\Delta\chi(T) = \Delta\chi_0 (1 - T/T_{NI})^m$ where $\Delta\chi_0$ is the limiting value of the order parameter, T_{NI} is the nematic-isotropic transition temperature and m is a fitting parameter capturing the steepness of the divergence and assumes a value of 0.22 in the Maier-Saupe mean-field approximation [28]. The characteristic time for alignment τ is given by the balance of viscosity $\eta(T)$ against the field interaction energy $F(\Delta\chi(T))$. Using a simple Arrhenius model, $\eta = \eta_0 \exp(E/k_B T)$ where E represents the energetic barrier to flow, and $F \sim \Delta\chi$ as discussed previously. Thus we expect τ as shown in Eq.2 and that the orientational order parameter which captures the degree of alignment evolves exponentially according to this timescale as $\langle P_2 \rangle \sim 1 - \exp(-t/\tau)$ [26, 29]. Any contributions from the influence of the field on the order parameter $\Delta\chi$ are small as discussed above and can be reasonably neglected.

$$\tau \sim \left(\frac{2\mu_0\eta_0}{\Delta\chi_0 B^2} \right) \frac{\exp(E/k_B T)}{(1 - T/T_{NI})^m} \quad (2)$$

It is clear that for a given annealing time, there will be an optimum temperature range over which $\langle P_2 \rangle$ is maximized, as shown in Fig. 4a,b in terms of normalized temperature $\tilde{T} = 1 - (T/T_{NI})$. This qualitative behavior is remarkably well captured experimentally. Samples were quenched from the disordered state to various temperatures below T_{ODT} and isothermally annealed at 6 T for 1 hour. The azimuthal variation of scattered intensity from the BCP microdomains is shown in Fig. 4c with the temperature dependence of the FWHM of Gaussian fits (Fig. 4d) where smaller FWHM are correlated with higher $\langle P_2 \rangle$. FWHM is used here as an internally consistent measure of the degree of alignment in preference to estimations of $\langle P_2 \rangle$ from the scattering data due to the sensitivity of this calculation to background subtraction.

From Fig. 4d it is apparent that viscosity strongly

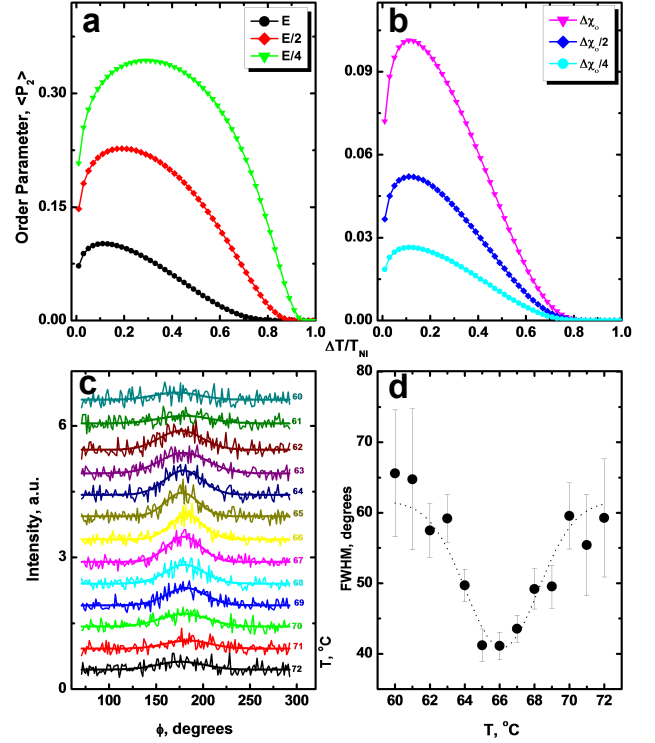


FIG. 4. a,b: $\langle P_2 \rangle$ dependence on annealing temperature at time $t = 0.1\tau_{\tilde{T}=0.05}$; $m = 0.22$, $(2\mu_0\eta_0/\Delta\chi_0 B^2) = 1$, $\Delta\chi_0 = 1$, $E/k_B T_{NI} = 1.5$. c: Azimuthal intensity variation for samples annealed at different temperatures. d: FWHM of azimuthal intensity. Line is a guide to the eye.

dominates in this system. The BCP has a very limited ability to respond to the field due to severe kinetic limitations starting only 6-8 °C below T_{ODT} . This suggests that the strong alignment observed in samples that were slowly cooled to 25 °C originates only due to the residence of the system within this small temperature range and not due to the continuous action of the field down to the final temperature. This is confirmed by samples which were zero-field quenched at ≈ 10 °C/min after an isothermal anneal for 1 hour at 5 T at 69 °C. As shown in Fig. 5, the system is only weakly ordered and aligned at 69 °C, but cooling to room temperature in the absence of the field produces a sharply aligned system with similar intensities and azimuthal FWHM as obtained during continuous cooling ramps of 0.1 °C/min (Fig. 1b). The weak alignment produced during the isothermal anneal is thus sufficient to bias or template the alignment of the system as it undergoes additional ordering on cooling, even in the absence of the field. We speculate that the intervening $N - SmA$ transition may underpin this orientation refinement, but further studies are required to properly address this interesting feature.

In summary, we have provided new results concerning the real-time response of LC BCPs under high magnetic fields. Our work shows that in these systems, there is no

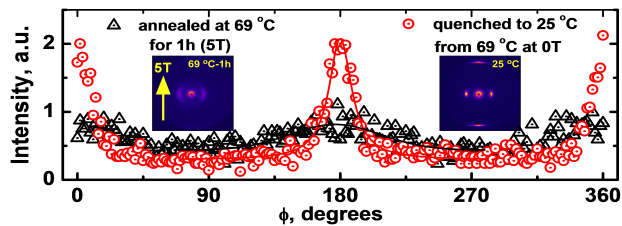


FIG. 5. Azimuthal intensity at 69 °C and on subsequent zero-field cooling to 25 °C with associated 2D SAXS data.

appreciable field effect on T_{ODT} up to field strengths of 6 T. We can reasonably account for this given the large enthalpy associated with the ODT relative to the field interaction energy. Time resolved measurements show that slow grain rotation is active as a mechanism for alignment during isothermal annealing experiments and that selective melting cannot play a substantive role. There is a severe kinetic limitation that arises a few °C below the ODT which results in a restricted range of temperatures over which field alignment of the microstructure can be reasonably advanced. Consistent with this, we observe that the action of the field in a small window near ODT is sufficient to template very strong alignment of the system on cooling in the absence of the field and is responsible for the alignment response of the system in general. Overall, these results demonstrate new capabilities for *in situ* study of block copolymer physics under large magnetic fields and have important implications for the design of schemes for directed self-assembly of these materials.

The authors thank Profs. E. Thomas, F. Bates and R. Segalman for fruitful discussions, Mike Degen (Rigaku Inc.) and AMI Inc. for technical support, and gratefully acknowledge NSF funding under DMR-0847534.

* manesh.gopinadhan@yale.edu

† pawel.majewski@yale.edu

‡ chinedum.osuji@yale.edu

[1] S. Darling, Prog. Polym. Sci. **32**, 1152 (2007).

[2] P. Majewski, M. Gopinadhan, and C. Osuji, J. Polym. Sci. Part B: Polym. Phys. (2012).

[3] M. I. Boamfa, K. Viertler, A. Wewerka, F. Stelzer, P. C. M. Christianen, and J. C. Maan, Phys. Rev. Lett.

90, 025501 (2003).

[4] C. Osuji, P. Ferreira, G. Mao, C. Ober, J. Vander Sande, and E. Thomas, Macromolecules **37**, 9903 (2004).

[5] I. W. Hamley, V. Castelletto, Z. B. Lu, C. T. Imrie, T. Itoh, and M. Al-Hussein, Macromolecules **37**, 4798 (2004).

[6] Y. Tao, H. Zohar, B. Olsen, and R. Segalman, Nano Lett. **7**, 2742 (2007).

[7] B. Xu, R. Piñol, M. Nono-Djamen, S. Pensec, P. Keller, P. Albouy, D. Lévy, and M. Li, Faraday Discuss. **143**, 235 (2009).

[8] M. Gopinadhan, P. Majewski, E. Beach, and C. Osuji, ACS Macro Lett. **1**, 184 (2012).

[9] T. Kimura, Polym. J. **35**, 823 (2003).

[10] T. Grigorova, S. Pispas, N. Hadjichristidis, and T. Thurn-Albrecht, Macromolecules **38**, 7430 (2005).

[11] A. Firouzi, D. Schaefer, S. Tolbert, G. Stucky, and B. Chmelka, J. Am. Chem. Soc. **119**, 9466 (1997).

[12] P. Majewski and C. Osuji, Soft Matter **5**, 3417 (2009).

[13] K. Wilmsmeyer, X. Zhang, and L. Madsen, Soft Matter **8**, 57 (2012).

[14] J. Vallooran, S. Bolisetty, and R. Mezzenga, Adv. Mater. (2011).

[15] W. Zheng and P. Hammond, Macromolecules **31**, 711 (1998).

[16] C. Rosenblatt, Phys. Rev. A **24**, 2236 (1981).

[17] W. Helfrich, Phys. Rev. Lett. **24**, 201 (1970).

[18] B. McCulloch, G. Portale, W. Bras, and R. A. Segalman, Macromolecules **44**, 7503 (2011).

[19] O. Francescangeli, F. Vita, F. Fauth, and E. T. Samulski, Phys. Rev. Lett. **107**, 207801 (2011).

[20] K. Koppi, M. Tirrell, F. Bates, K. Almdal, K. Almdal, and R. Colby, J. Phys. II **2**, 1941 (1992).

[21] K. Amundson, E. Helfand, X. Quan, S. Hudson, and S. Smith, Macromolecules **27**, 6559 (1994).

[22] A. Böker, H. Elbs, H. Hänsel, A. Knoll, S. Ludwigs, H. Zettl, V. Urban, V. Abetz, A. H. E. Müller, and G. Krausch, Phys. Rev. Lett. **89**, 135502 (2002).

[23] C. Liedel, C. W. Pester, M. Ruppel, V. S. Urban, and A. Böker, Macromol. Chem. Phys. **213**, 259 (2012).

[24] Y. Cohen, R. Albalak, B. Dair, M. Capel, and E. Thomas, Macromolecules **33**, 6502 (2000).

[25] A. Makke, M. Perez, O. Lame, and J. Barrat, Proc. Natl. Acad. Sci. **109**, 680 (2012).

[26] A. Böker, H. Elbs, H. Hänsel, A. Knoll, S. Ludwigs, H. Zettl, A. Zvelindovsky, G. Sevink, V. Urban, V. Abetz, et al., Macromolecules **36**, 8078 (2003).

[27] I. Haller, Prog. Solid State Chem. **10**, 103 (1975).

[28] R. J. A. Tough and M. J. Bradshaw, J. Phys. **44**, 447 (1983).

[29] K. Schmidt, H. Schoberth, F. Schubert, H. Hänsel, F. Fischer, T. Weiss, G. Sevink, A. Zvelindovsky, A. Böker, and G. Krausch, Soft Matter **3**, 448 (2007).